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(54) REFRIGERANT COMPOSITIONS

KÜHLMITTELZUSAMMENSETZUNG

COMPOSITIONS REFRIGERANTES

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Description

[0001] The present invention relates to refrigerant compositions, particularly for use as replacements in refrigeration equipment currently employing, or designed to employ, the refrigerant R22.

[0002] Refrigerant R22 ($CClF_2$) has been principally used as a refrigerant for air conditioning systems. However, R22 contains chlorine atoms and has been implicated in environmental damage to the ozone layer. As a result efforts have been made to replace R22 with a refrigerant formulation which does not involve the use of refrigerants such as R22 which contain chlorine atoms.

[0003] Among alternatives, particular attention has been directed at R134a($C_2H_2F_4$;1,1,1,2-tetrafluoroethane) along with pentafluoroethane (R125) (b.pt. -48.6°C). Commercial formulations of these two refrigerants involve the use of a hydrocarbon, namely propane, propylene or isobutane. While these refrigerant formulations are generally effective as replacements for R22, nevertheless it has been found that their use is not entirely satisfactory.

[0004] Difficulty has arisen with the flammability of the fractionated composition, that is to say the vapour above the liquid composition possesses flammability problems. As a result these commercial formulations can produce flammable compositions under some leak scenario conditions. The flammability of these refrigerant compositions resides in their hydrocarbon content. One of the purposes of incorporating the hydrocarbon is so that formulation is compatible with the lubricants ordinarily used in R22 refrigeration equipment. The specific hydrocarbons have been selected because they possess the correct boiling point in relation to that of the fluorocarbon.

[0005] It has now been found, surprisingly, according to the present invention, that if a hydrocarbon with at least 4 carbon atoms other than methyl propane isobutane is used instead of those previously advocated the flammability of the fractionated composition is greatly reduced. This result is very surprising as n-butane, for example, has a significantly higher boiling point (-0.5°C) than, say, isobutane (-11.7°C) and is accordingly less volatile. Indeed, the U.S. NIST (National Institute of Standards & Technology) computer programs REFPREP and REFLEAK have predicted that at particularly preferred such n-butane-containing formulation would be flammable when it has been found not to be. Further, although there can be a considerable boiling point range between the lowest boiling point component and the hydrocarbon of the composition the temperature glide of the blend is relatively small. In a particular embodiment, although the boiling point range is 36.2°C, the temperature glide is only 3.9K at the boiling point of -34.6°C at one atmosphere pressure. It is further surprising that such a formulation has a reduced flammability because n-butane, for example, has a larger range of flammability limits as compared with isobutane. Thus-n-butane has a flammability range from 1.5 to 10.1% v/v whereas for isobutane it is only 1.7 to 9.7% v/v.

[0006] According to the present invention there is provided a refrigerant composition which comprises

(i) R125, R134a, R134 (1,1,2,2-tetrafluoroethane), 1,1-difluoroethane (R152a; b.pt. -24.7°C), 1,1,1,2,3,3,3-heptafluoropropane (R227ea; b.pt. -18.3°C) or 1,1,1,2,2,3,3-heptafluoropropane (R227ca; b.pt. -16.3°C), or a mixture of two or more thereof, in Embodiment A in an amount from 30 to 50% by weight, and in Embodiment B in an amount from 50 to 75% by weight, based on the weight of the composition and
(ii) an unsubstituted hydrocarbon of the formula C_nH_m in which n is at least 4 and m is at least 2n-2, other than methyl propane in an amount from 1 to 10% by weight based on the weight of the composition,

with the remainder, not exceeding 60% by weight based on the weight of the composition, being

(iii) R125, trifluoromethoxy-difluoromethane (b.pt. -34.6°C) or hexafluoro-cyclopropane (b.pt. - 31.5°C), or a mixture of two or more thereof.

The present invention also provides, as Embodiment C a refrigerant composition which comprises:-

(i) 1,1,1,2- or 1,1,2,2-tetrafluoroethane, or a mixture of pentafluoroethane and 1,1,1,2- or 1,1,2,2- tetrafluoroethane in an amount from 30 to 94% by weight based on the weight of the composition.
(ii) an unsubstituted hydrocarbon of the formula C_nH_m in which n is at least 4 and m is at least 2n-2, other than methyl propane, in an amount from 1 to 4% by weight based on the weight of the composition and
(iii) pentafluoroethane in an amount from 5 to 60% by weight based on the weight of the composition with the proviso that the concentration of pentafluoroethane in the composition is not 5 to 20% by weight based on the weight of the composition.

[0007] The present invention also provides a process for producing refrigeration which comprises evaporating a composition of the present invention in the vicinity of a body to be cooled. The invention also provides a refrigeration apparatus containing, as refrigerant, a composition of the present invention. The invention further provides the use of a refrigeration composition which comprises:

(i) pentafluoroethane, 1,1,1,2- or 1,1,2,2-tetrafluoroethane, 1,1-difluoroethane, trifluoromethoxypenta fluoroethane, 1,1,1,2,3,3,3,- heptafluoropropane or 1,1,1,2,2,3,3,-heptafluoropropane, or a mixture of two or more thereof, in an amount from 30 to 94% by weight based on the weight of the composition

(ii) an unsubstituted hydrocarbon of the formula C_nH_m in which n is at least 4 and m is at least 2n-2, other than methyl propane, in an amount from 1 to 10% by weight based on the weight of the composition, as a replacement for chlorodifluoromethane and

(iii) pentafluoroethane in an amount from 5 to 60% by weight based on the weight of the composition, as Embodiment D.

[0008] Component (ii) will be present in amount from 1 to 10%, especially 1 to 8%, preferably 2 to 6% and more preferably 2 to 5%, and in particular 2 or 3 to 4%, most preferably about 3.5%, by weight of the composition but only 1 to 4% in Embodiments A, B and C.

[0009] It will be appreciated that component (i) and component (iii) can both be R125. In this situation the composition can, therefore, be binary and the amount of R125 will be from 90 to 99% by weight. In all other situations the composition will be at least ternary.

[0010] Among the preferred compositions of the present invention are those which contain one or more of R125, R134a and R218. Thus component (iii) preferably comprises R125 and/or R128 while component (i) preferably comprises R125 and/or R134a.

[0011] In Embodiments A and B component (iii) represents the remainder of the composition (to 100%). Component (iii) is present in Embodiments C and D in an amount from 5 to 60% by weight, generally 5 to 50% by weight. If R125 does not form part of component (iii) then the amount will typically be from 5 to 20%, especially 5 to 15% and preferably 7 to 12%, by weight. It will be appreciated that if the composition contains R125, the concentration of R125 can be split between components (iii) and (i). Thus in Embodiment C the concentration of R125 in the composition is not 5 to 20% by weight based on the weight of the composition.

[0012] The concentration of component (i) is from 30 to 50% by weight in Embodiment A and 50 to 75%, by weight in Embodiment B. In Embodiment C and D the concentration is from 30 to 94% by weight, generally 50 to 90% and especially 75 to 90%, by weight.

[0013] Typically hydrocarbons which can be employed as component (ii), and which may be saturated or unsaturated, possess 4 or 5 carbon atoms and include methylenecyclopropane, 1-butene, cis and trans-2-butene, butane, cyclobutane, cyclopentene, cyclopentane, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1-pentene, cis and trans-2-pentene, 2-methylbutane, pentane and mixtures of two or more thereof. The use of n-butane (R600) is particularly preferred.

[0014] Specific formulations which have been found to be effective are as follows:

	% by weight		% by weight	
			(a)	(b)
R218	9	R125	46	46.5
R134a	88		50	50
n-butane	3		4	3.5

[0015] The following Examples further illustrate the present invention; Examples 2,3 and 5 are included for comparison.

Worst case fractionation study:

[0016] The apparatus used for these determinations consisted of a small stainless steel cylinder (343 cm^3 internal volume) which was charged with the blend under evaluation in various fill ratios and was then placed in a temperature controlled bath brought to the appropriate temperature and allowed to equilibrate for at least 30 minutes. The temperature in the bath was controlled to within 0.1°C and was monitored with a platinum resistance thermometer. Once equilibrated a 75 cm^3 sample cylinder was attached to the test cylinder using quick connections and the void spaces between the test cylinder and the sample cylinder evacuated with a vacuum pump. The system was left for at least 15 minutes to check for leaks and then vapour from the test cylinder was slowly introduced into the sample cylinder using a metering valve. Once the pressure in the sample cylinder reached 1 atmosphere the introduction was stopped, the two cylinders isolated and then the sample cylinder was removed for analyses by GLC. The GLC was calibrated using three separate analyses of a standard which were made up in such a way as to be quite close to the vapour composition expected for the test mixture. This sampling was repeated and a duplicate sample analysed on the GLC. This was

repeated at various temperatures with various fill ratios and the worst case result was the one with the highest hydrocarbon content.

[0017] The results obtained as shown below. The flammability tests, determined using the method detailed in ASTM E 681-85, show that the formulations of Examples 1 and 4 are significantly superior to those of Examples 2, 3 and 5, while possessing good refrigeration performance. It will be noted that the vapour of the composition of Example 1 (and 4) was non-flammable. It is clear that similar comments apply to the composition R125 - 46.5%, R134A - 50% and R600 - 3.5%.

	Liquid Composition % w/w				
	R125	R218	R134a	R600a	R600
Example 1	46	-	50	-	4
Example 2	46	-	50	4	-
Example 3	46.5	-	50	3.5	-
Example 4	-	9	88	-	3
Example 5	-	9	88	3	-

Refrigeration Performance as an alternative to R22

Evaporator Temperature / °C	Refrigeration Effect / kW				Coefficient of Performance			
	R22	Example 1	Example 2	Example 3	R22	Example 1	Example 2	Example 3
-15	0.932	0.855	0.823	0.711	1.269	1.204	1.194	0.966
-10	1.328	1.124	1.133	1.058	1.492	1.443	1.436	1.323
-5	1.723	1.437	1.476	1.413	1.716	1.700	1.695	1,624
0	2.118	1.796	1.852	1.775	1.939	1.976	1.970	1.869
5	2.513	2.200	2.262	2.145	2.163	2.270	2.262	2.058

Refrigeration Performance as an alternative to R12

Evaporator Temperature /°C	Refrigeration Effect / kW			Coefficient of Performance		
	R12	Example 4	Example 5	R12	Example 4	Example 5
-15	0.585	0.706	0.738	0.942	1.002	1.036
-10	0.786	0.877	0.889	1.227	1.312	1.314
-5	1.018	1.119	1.128	1.513	1.623	1.591
0	1.281	1.434	1.453	1.799	1.933	1.869
5	1.575	1.820	1.865	2.085	2.244	2.146

Fractionation and Flammability test results

Blend	Fractionated Vapour Composition / % w/w					Lower Flammable Limit % v/v in Air
	R125	R218	R134a	R600a	R600	
Example 1	60.7	-	34.6	-	4.7	Non Flammable
Example 2	64.4	-	29.1	6.5	-	12
Example 3	64.7	-	29.8	5.5	-	15
Example 4	-	22.9	72.5	-	4.6	Non Flammable
Example 5	-	21.5	72.5	6	-	9

Claims

1. A refrigerant composition which comprises:

   (i) pentafluoroethane, 1,1,1,2- or 1,1,2,2-tetrafluoroethane, 1,1-difluoroethane; trifluoromethoxypentafluoroethane, 1,1,1,2,3,3,3-heptafluoropropane or 1,1,1,2,2,3,3-heptafluoropropane, or a mixture of two or more thereof, in an amount from 30 to 50% by weight based on the weight of the composition
   (ii) an unsubstituted hydrocarbon of the formula C_nH_m in which n is at least 4 and m is at least 2n-2, other than methyl propane, in an amount from 1 to 4% by weight based on the weight of the composition.

   with the remainder, not exceeding 60% by weight based on the weight of the compostion, being:

   (iii) pentafluoroethane, trifluoromethoxydifluoromethane or hexafluorocyclopropane, or a mixture of two or more thereof.

2. A composition according to claim 1 wherein component (i) is present in an amount of 50% by weight based on the weight of the composition.

3. A composition according to claim 1 or 2 wherein component (i) is 1,1,1,2-tetrafluoroethane or a mixture of said ethane with pentafluoroethane.

4. A refrigerant composition which comprises:

   (i) pentafluoroethane, 1,1,1,2- or 1,1,2,2-tetrafluoroethane, 1,1-difluoroethane, trifluoromethoxypentafluoroethane, 1,1,1,2,3,3,3-heptafluoropropane or 1,1,1,2,2,3,3-heptafluoropropane, or a mixture of two or more thereof, in an amount from 50 to 75% by weight based on the weight of the composition
   (ii) an unsubstituted hydrocarbon of the formula C_nH_m in which n is at least 4 and m is at least 2n-2, other than methyl propane, in an amount from 1 to 4% by weight based on the weight of the composition; with the remainder being
   (iii) pentafluorethane, trifluoromethoxydifluoromethane or hexafluorocyclopropane, or a mixture of two or more thereof.

5. A composition according to claim 4 wherein component (i) is 1,1,1,2-tetrafluoroethane or a mixture of said ethane with pentafluoroethane.

6. A composition according to claim 4 or 5 wherein component (iii) is pentafluoroethane.

7. A refrigerant composition which comprises:-

   (i) 1,1,1,2- or 1,1,2,2-tetrafluoroethane, or a mixture of pentafluoroethane and 1,1,1,2- or 1,1,2,2- tetrafluoroethane, in an amount from 30 to 94% by weight based on the weight of the composition,
   (ii) an unsubstituted hydrocarbon of the formula C_nH_m in which n is at least and m is at least 2n-2, other than methyl propane, in an amount from 1 to 4% by weight based on the weight of the composition,
   (iii) pentafluoroethane in an amount from 5 to 60% by weight based on the weight of the composition with the proviso that the concentration of pentafluoro-ethane in the composition is not 5 to 20% by weight based on

the weight of the composition.

8. A composition according to any one of the preceding claims wherein component (ii) is present in an amount from 2 to 4% by weight based on the weight of the composition.

9. A composition according to claim 8 wherein component (ii) is present in an amount from 3 to 4% by weight based on the weight of the composition.

10. A composition according to any one of the preceding claims wherein component (ii) is a mixture of said hydrocarbons.

11. A composition according to any one of the preceding claims wherein component (ii) comprises a hydrocarbon which possesses 4 or 5 carbon atoms.

12. A composition according to claim 11 wherein component (ii) comprises a hydrocarbon which is n-butane.

13. A composition according to claim 12 which comprises:

(a) 46 to 46.5% by weight of pentafluoroethane
(b) 50 % by weight of 1,1,1,3-tetrafluoroethane and
(c) 4 to 3.5% by weight, respectively, of n-butane.

14. Use as a refrigerant of a composition as claimed in any one of claims 1 to 13.

15. Use according to claim 14 in a refrigeration or airconditioning system designed to use chlorodifluoromethane as refrigerant.

16. Use of a refrigeration composition which comprises:

(i) pentafluorethane, 1,1,1,2- or 1,1,2,2-tetrafluoroethane, 1,1-difluoroethane, 1,1,1,2,3,3,3,- heptafluoropropane or 1,1,1,2,2,3,3,-heptafluoropropane, or a mixture of two or more thereof, in an amount from 30 to 94% by weight based on the weight of the composition and
(ii) an unsubstituted hydrocarbon of the formula C_nH_m in which n is at least 4 and m is at least 2n-2, other than methyl propane, in an amount from 1 to 10% by weight based on the weight of the composition, as a replacement for chlorodifluoromethane.
(iii) pentafluoroethane in an amount from 5 to 60% by weight based on the weight of the composition, as a replacement for chlorodifluoromethane.

17. Use according to claim 16 wherein the composition is as defined in claim 13.

18. The process for producing refrigeration which comprises evaporating a composition as claimed in any one of claims 1 to 13 in the vicinity of a body to be cooled.

19. A refrigeration apparatus containing, as refrigerant, a composition as claimed in any one of claims 1 to 13.

20. A refrigeration apparatus according to claim 19 which is designed to use chlorodifluoromethane as refrigerant.

Patentansprüche

1. Eine Kühlmittelzusammensetzung, welche umfasst:

(i) Pentafluorethan, 1,1,1,2- oder 1,1,2,2-Tetrafluorethan, 1,1-Difluorethan, Trifluormethoxypentafluorethan, 1,1,1,2,3,3,3-Heptafluorpropan oder 1,1,1,2,2,3,3-Heptafluorpropan oder eine Mischung aus zwei oder mehreren von diesen in einer Menge von 30 bis 50 Gew.-%, bezogen auf das Gewicht der Zusammensetzung,

(ii) einen unsubstituierten Kohlenwasserstoff der Formel C_nH_m, bei welchem n wenigstens 4 ist und m wenigstens 2n-2 ist, ausgenommen Methylpropan, in einer Menge von 1 bis 4 Gew.-%, bezogen auf das Gewicht

der Zusammensetzung,

wobei der Rest, welcher 60 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, nicht überschreitet, ist:

(iii) Pentafluorethan, Trifluormethoxydifluormethan oder Hexafluorcyclopropan oder eine Mischung aus zwei oder mehreren von diesen.

2. Eine Zusammensetzung gemäß Anspruch 1, wobei die Komponente (i) in einer Menge von 50 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, vorliegt.

3. Eine Zusammensetzung gemäß Anspruch 1 oder 2, wobei die Komponente (i) 1,1,1,2-Tetrafluorethan oder eine Mischung des genannten Ethans mit Pentafluorethan ist.

4. Eine Kühlmittelzusammensetzung, welche umfasst:

(i) Pentafluorethan, 1,1,1,2- oder 1,1,2,2-Tetrafluorethan, 1,1-Difluorethan, Trifluormethoxypentafluorethan, 1,1,1,2,3,3,3-Heptafluorpropan oder 1,1,1,2,2,3,3-Heptafluorpropan oder eine Mischung aus zwei oder mehreren von diesen, in einer Menge von 50 bis 75 Gew.-%, bezogen auf das Gewicht der Zusammensetzung,

(ii) einen unsubstituierten Kohlenwasserstoff der Formel C_nH_m, bei welchem n wenigstens 4 ist und m wenigstens 2n-2 ist, ausgenommen Methylpropan, in einer Menge von 1 bis 4 Gew.-%, bezogen auf das Gewicht der Zusammensetzung; wobei der Rest ist:

(iii) Pentafluorethan, Trifluormethoxydifluormethan oder Hexafluorcyclopropan oder eine Mischung aus zwei oder mehreren von diesen.

5. Eine Zusammensetzung gemäß Anspruch 4, wobei die Komponente (i) 1,1,1,2-Tetrafluorethan oder eine Mischung des genannten Ethans mit Pentafluorethan ist.

6. Eine Zusammensetzung gemäß Anspruch 4 oder 5, wobei die Komponente (iii) Pentafluorethan ist.

7. Eine Kühlmittelzusammensetzung, welche umfasst:

(i) 1,1,1,2- oder 1,1,2,2-Tetrafluorethan oder eine Mischung aus Pentafluorethan und 1,1,1,2- oder 1,1,2,2-Tetrafluorethan in einer Menge von 30 bis 94 Gew.-%, bezogen auf das Gewicht der Zusammensetzung,

(ii) einen unsubstituierten Kohlenwasserstoff der Formel C_nH_m, bei welchem n wenigstens 4 ist und m wenigstens 2n-2 ist, ausgenommen Methylpropan, in einer Menge von 1 bis 4 Gew.-%, bezogen auf das Gewicht der Zusammensetzung,

(iii) Pentafluorethan in eine Menge von 5 bis 60 Gew.-%, bezogen auf das Gewicht der Zusammensetzung unter der Voraussetzung, dass die Konzentration von Pentafluorethan in der Zusammensetzung nicht 5 bis 20 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, beträgt.

8. Eine Zusammensetzung gemäß irgendeinem der vorhergehenden Ansprüche, wobei die Komponente (ii) in einer Menge von 2 bis 4 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, vorliegt.

9. Eine Zusammensetzung gemäß Anspruch 8, wobei die Komponente (ii) in einer Menge von 3 bis 4 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, vorliegt.

10. Eine Zusammensetzung gemäß irgendeinem der vorhergehenden Ansprüche, wobei die Komponente (ii) eine Mischung der genannten Kohlenwasserstoffe ist.

11. Eine Zusammensetzung gemäß irgendeinem der vorhergehenden Ansprüche, wobei die Komponente (ii) einen Kohlenwasserstoff umfasst, welcher 4 oder 5 Kohlenstoffatome besitzt.

12. Eine Zusammensetzung gemäß Anspruch 11, wobei die Komponente (ii) einen Kohlenwasserstoff umfasst, welcher n-Butan ist.

13. Eine Zusammensetzung gemäß Anspruch 12, welche umfasst:

    (a) 46 bis 46,5 Gew.-% Pentafluorethan,
    (b) 50 Gew.-% 1,1,1,3-Tetrafluorethan und
    (c) entsprechend 4 bis 3,5 Gew.-% n-Butan.

14. Verwendung einer Zusammensetzung, wie sie in irgendeinem der Ansprüche 1 bis 13 beansprucht ist, als Kühlmittel.

15. Verwendung gemäß Anspruch 14 in einem Kühlungs- oder Klimatisierungssystem, das zur Verwendung von Chlordifluormethan als Kühlmittel ausgelegt ist.

16. Verwendung einer Kühlzusammensetzung, welche umfasst:

    (i) Pentafluorethan, 1,1,1,2- oder 1,1,2,2-Tetrafluorethan, 1,1-Difluorethan, 1,1,1,2,3,3,3-Heptafluorpropan oder 1,1,1,2,2,3,3-Heptafluorpropan oder eine Mischung aus zwei oder mehreren von diesen in einer Menge von 30 bis 94 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, und

    (ii) einen unsubstituierten Kohlenwasserstoff der Formel C_nH_m, bei welchem n wenigstens 4 ist und m wenigstens 2n-2 ist, ausgenommen Methylpropan, in einer Menge von 1 bis 10 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, als Ersatz für Chlordifluormethan,

    (iii) Pentafluorethan in einer Menge von 5 bis 60 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, als Ersatz für Chlordifluormethan.

17. Verwendung gemäß Anspruch 16, wobei die Zusammensetzung wie in Anspruch 13 definiert ist.

18. Das Verfahren zur Erzeugung einer Kühlung, welches das Verdunsten einer Zusammensetzung, wie sie in irgendeinem der Ansprüche 1 bis 13 beansprucht wird, in der Nähe eines abzukühlenden Körpers umfasst.

19. Ein Kühlgerät, welches als Kühlmittel eine Zusammensetzung, wie sie in irgendeinem der Ansprüche 1 bis 13 beansprucht wird, umfasst.

20. Ein Kühlgerät gemäß Anspruch 19, welches zur Verwendung von Chlordifluormethan als Kühlmittel ausgelegt ist.

Revendications

1. Composition réfrigérante qui comprend :

    (i) le pentafluoroéthane, le 1,1,1,2- ou le 1,1,2,2-tétrafluoroéthane, le 1,1-difluoroéthane, le trifluorométhoxypentafluoroéthane, le 1,1,1,2,3,3,3-heptafluoropropane ou le 1,1,1,2,2,3,3-heptafluoropropane, ou un mélange de deux ou plus de ceux-ci, dans une quantité de 30 à 50 % par poids sur la base du poids de la composition,
    (ii) un hydrocarbure qui n'est pas substitué de formule C_nH_m dans lequel n vaut au moins 4 et m vaut au moins 2n-2, autre que le méthylpropane, dans une quantité de 1 à 4 % par poids sur la base du poids de la composition, avec le reste, n'excédant pas 60 % par poids sur la base du poids de la composition, étant
    (iii) le pentafluoroéthane, le trifluorométhoxydifluorométhane ou l'hexafluorocyclopropane, ou un mélange de deux ou plus de ceux-ci.

2. Composition selon la revendication 1, dans laquelle le composé (i) est présent dans une quantité de 50 % par poids sur la base du poids de la composition.

3. Composition selon les revendications 1 ou 2, dans laquelle le composé (i) est le 1,1,1,2-tétrafluoroéthane ou un mélange dudit éthane avec le pentafluoroéthane.

4. Composition réfrigérante qui comprend :

    (i) le pentafluoroéthane, le 1,1,1,2- ou le 1,1,2,2-tétrafluoroéthane, le 1,1-difluoroéthane, le trifluorométhoxy-

pentafluoroéthane, le 1,1,1,2,3,3,3-heptafluoropropane ou le 1,1,1,2,2,3,3-heptafluoropropane, ou un mélange de deux ou plus de ceux-ci, dans une quantité de 50 à 75 % par poids sur la base du poids de la composition,
(ii) un hydrocarbure qui n'est pas substitué de formule C_nH_m dans lequel n vaut au moins 4 et m vaut au moins 2n-2, autre que le méthylpropane, dans une quantité de 1 à 4 % par poids sur la base du poids de la composition ; avec le reste étant
(iii) le pentafluoroéthane, le trifluorométhoxydifluorométhane ou l'hexarluorocyclopropane, ou un mélange de deux ou plus de ceux-ci.

5. Composition selon la revendication 4, dans laquelle le composé (i) est le 1,1,1,2-tétrafluoroéthane ou un mélange dudit éthane avec le pentafluoroéthane.

6. Composition selon les revendications 4 ou 5, dans laquelle le composé (iii) est le pentafluoroéthane.

7. Composition réfrigérante qui comprend :

(i) le 1,1,1,2- ou le 1,1,2,2-tétrafluoroéthane, ou un mélange de pentafluoroéthane et de 1,1,1,2- ou de 1,1,2,2-tétrafluoroéthane, dans une quantité de 30 à 94 % par poids sur la base du poids de la composition,
(ii) un hydrocarbure qui n'est pas substitué de formule C_nH_m dans lequel n vaut au moins 4 et m vaut au moins 2n-2, autre que le méthylpropane, dans une quantité de 1 à 4 % par poids sur la base du poids de la composition, avec le reste étant
(iii) le pentafluoroéthane, dans une quantité de 5 à 60 % par poids sur la base du poids de la composition à condition que la concentration en pentafluoroéthane dans la composition ne soit pas de 5 à 20 % par poids sur la base du poids de la composition.

8. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composé (ii) est présent dans une quantité de 2 à 4 % par poids sur la base du poids de la composition.

9. Composition selon la revendication 8, dans laquelle le composé (ii) est présent dans une quantité de 3 à 4 % par poids sur la base du poids de la composition.

10. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composé (ii) est un mélange desdits hydrocarbures.

11. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composé (ii) comprend un hydrocarbure qui possède 4 ou 5 atomes de carbone.

12. Composition selon la revendication 11, dans laquelle le composé (ii) comprend un hydrocarbure qui est le n-butane.

13. Composition selon la revendication 12 qui comprend :

(a) 46 à 46,5 % par poids de pentafluoroéthane
(b) 50 % par poids de 1,1,1,3-tétrafluoroéthane et
(c) respectivement 4 et 3,5 % par poids de n-butane

14. Utilisation d'une composition réfrigérante selon l'une quelconque des revendications 1 à 13.

15. Utilisation selon la revendication 14 dans un système de réfrigération ou d'air conditionné créé pour utiliser le chlorodifluorométhane en tant que réfrigérant.

16. Utilisation d'une composition réfrigérante qui comprend :

(i) le pentafluoroéthane, le 1,1,1,2- ou le 1,1,2,2-tétrafluoroéthane, le 1,1-difluoroéthane, le 1,1,1,2,3,3,3-heptafluoropropane ou le 1,1,1,2,2,3,3-heptafluoropropane, ou un mélange de deux ou plus de ceux-ci, dans une quantité de 30 à 94 % par poids sur la base du poids de la composition, et
(ii) un hydrocarbure qui n'est pas substitué de formule C_nH_m dans lequel n vaut au moins 4 et m vaut au moins 2n-2, autre que le méthylpropane, dans une quantité de 1 à 10 % par poids sur la base du poids de la composition, en tant que remplacement pour le chlorodifluorométhane,
(iii) le pentafluoroéthane, dans une quantité de 5 à 60 % par poids sur la base du poids de la composition, en

tant que remplacement pour le chlorodifluorométhane.

17. Utilisation selon la revendication 16, dans laquelle la composition est telle que définie dans la revendication 13.

18. Procédé pour produire de la réfrigération qui comprenne l'étape consistant à évaporer une composition selon l'une quelconque des revendications 1 à 13 dans la proximité d'un corps à refroidir.

19. Appareil de réfrigération contenant, en tant que réfrigérant, une composition selon l'une quelconque des revendications 1 à 13.

20. Appareil de réfrigération selon la revendication 19, qui est créé pour utiliser le chlorodifluorométhane en tant que réfrigérant.